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Mechanism of the Gas-phase Oxidation of Propylene in a Propylene-excess Atmosphere under Pressure*[1]

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The mechanism of the oxidation of propylene is studied through the addition of *t*-butyl hydroperoxide, acetaldehyde, or propionaldehyde to the reactant (propylene and oxygen), and also through the direct addition of the products of the ($C_3H_5Br+O_2$ or CH_3CHO+O_2) reaction to propylene. The following conclusions are reached: acetaldehyde and not propionaldehyde is responsible for chain-branching, acetaldehyde is formed from the allyl peroxy radical alone, propylene oxide is formed mainly by the reaction of the acetyl peroxy radical with propylene, the allyl peroxy radical probably contributes to the formation of propylene oxide, propionaldehyde, and acrolein in an equal extent, and the recombination of radicals is highly retarded in this propylene-excess system. On the basis of the data obtained, a plausible reaction scheme is proposed.

The data presented in a previous paper[1) have demonstrated the negative temperature coefficient[2,3a) in the conversion of propylene and in the yields of all the products except carbon dioxide, and have also demonstrated that excess propylene is essential to obtaining the high yields of acetaldehyde and propylene oxide in the thermal oxidation of propylene with an inert fluidized bed reactor under pressure.

The mechanism of the oxidation of hydrocarbons is generally known to be a degenerate branching process accompanying the negative temperature coefficient.[2,3a) Concerning the branching agent in the low-temperature oxidation of propylene, higher aldehydes contribute to the degenerate branching process according to Mulcahy and Ridge[4) and also according to Batten and Ridge.[5) Among the higher aldehydes, acrolein is not a branching agent according to Mullen and Skirrow.[6) It has been concluded that only acetaldehyde is responsible for the branching process,[3b,4-6) however, the role of propionaldehyde has not yet been discussed. And the formation of acetaldehyde through the isomerization of the allyl peroxy radical was discussed by Shtern and Polyak.[3b)

The features of the oxidation of propylene can be explained by the proposed formation of the unreactive allyl radical according to Mullen and Skirrow.[6)

Contrary to the results presented above[3b,4-6) propylene oxide is one of the major products in the propylene oxidation in a propylene-excess atmosphere under pressure.[1,7) The scheme of the reaction was duscussed first by Kamiya *et al.*[8) Some parts of the reaction scheme were elucidated using carbon-14-labeled propylene by White, Davis, and Hammack.[9) Propylene oxide and propionaldehyde were considered by Cvetanović[10) to be formed through the addition of an oxygen atom to the double bond of propylene. Oba and Sakai recently demonstrated that the methyl group of propylene was retained in the resulting propylene oxide.[11)

The purpose of the present work is to obtain some experimentally probable views on the main routes of the reaction. Two kinds of experiments will be described. In the first (Exp. A), *t*-butyl hydroperoxide, acetaldehyde, or propionaldehyde

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1) E. Echigoya, M. Masai and K. Morikawa, This Bulletin, **41**, 904 (1968).

2) R. Ben-Aïn and M. Lucquin, "Oxidation and Combustion Reviews," Vol. 1, ed. by C. F. R. Tipper, Elsevier Pub. Co., Amsterdam (1965), p. 1.

3) V. Ya. Shtern, "The Gas-phase Oxidation of Hydrocarbons," translated by M. F. Mullins: 3a) pp. 105—110, 480—492; 3b) pp. 527—573, Pergamon Press, Oxford (1964).

4) M. F. R. Mulcahy and M. J. Ridge, *Trans. Faraday Soc.*, **49**, 906 (1953).

5) J. Batten and M. J. Ridge, *Australian J. Chem.*, **8**, 370 (1955).

6) J. D. Mullen and G. Skirrow, *Proc. Roy. Soc.*, **A244**, 312 (1958).

7) Y. Kamiya, *Sekiyu Gakkai Shi (J. Japan Petrol. Inst.)*, **5**, 18 (1962).

8) Y. Kamiya, N. Sekine and Y. Yamakawa, *ibid.*, **8**, 951 (1965).

9) E. R. White, H. G. Davis and E. S. Hammack, *J. Am. Chem. Soc.*, **87**, 1175 (1965).

10) R. J. Cvetanović, *Can. J. Chem.*, **36**, 623 (1958); S. Sato and R. J. Cvetanović, *ibid.*, **37**, 953 (1959).

11) S. Oba and W. Sakai, This Bulletin, **40**, 681 (1967).

is added to the reactant gas (propylene gas and oxygen); in the second (Exp. B), the oxidation products of allyl bromide or acetaldehyde are added directly to the propylene gas. The following conclusions are obtained: acetaldehyde and not propionaldehyde is the branching agent in this reaction; acetaldehyde is formed from the allyl peroxy radical; propylene oxide is formed mainly through the addition of the acetyl peroxy radical to the double bond of propylene; the allyl peroxy radical contributes to the formation of propylene oxide, propionaldehyde, and acrolein to an equal extent, and the recombination of radicals is highly retarded by the excess propylene. A plausible reaction scheme is proposed on the basis of the data obtained here.

Experimental

Materials. The propylene gas and oxygen have been described before.[1] The acetaldehyde was prepared by the depolymerization of paraldehyde and distilled just before use. Allyl bromide of a G. R. quality was obtained from the Tokyo Kasei Kogyo Co., Ltd. (Tokyo). *t*-Butyl hydroperoxide of a 70% purity was obtained from the Lucidol-Yoshitomi Co., Ltd. (Osaka). Propionaldehyde of an E. P. quality was obtained from the Tokyo Kasei Kogyo Co., Ltd. The silicon carbide has been described before.[1]

Reactors. Two kinds of reaction experiments were carried out using two different reactors.

For Exp. A. The oxidation experiments featuring the addition of *t*-butyl hydroperoxide, acetaldehyde, or propionaldehyde to the reactant gas (propylene and oxygen) were carried out in a fluidized bed reactor, shown in Fig. 1. The reactor was made of stainless steel*[3] and had the following dimensions; 24.5 mm i. d.×460 mm length. It contained 70 cc of silicon carbide (150—250 Tyler mesh) as a fluidizing powder. The quiescent bed height was 200 mm. The mixer (evaporator), made of steel had the following dimensions; 20 mm i. d.×150 mm length. It contained quartz chips washed with diluted nitric acid.

For Exp. B. The reaction of propylene with the products of the $C_3H_5Br+O_2$ or CH_3CHO+O_2 reaction was carried out in the reaction apparatus shown in Fig. 2. The reactor, made of stainless steel,*[3] consisted of two concentric tubes. The inner tubes, in which the oxidation of allyl bromide or acetaldehyde was carried out, had the following dimensions; 8 mm o. d. × 6 mm i. d. × 300 mm length. The outer tube, in which the reactions of propylene with the products from the inner tube were carried out, had the following dimensions; 24.5 mm i. d. × 360 mm length. The volume of the effective reaction zone in the inner tube was about 1.0 cc, while the volume of the effective reaction zone in the outer tube was about 46 cc. The reactor was heated from the outside; the temperature of the inner tube was higher than that of the outer tube by 5—10°C during the experiments.

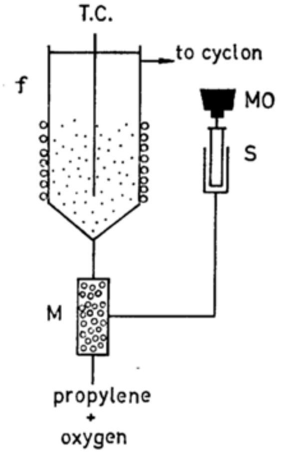

Fig. 1. Reactor for Exp. A.
f, fluidized bed reactor; M, mixer; MO, slow geared motor; S, syringe; T. C., thermocouple

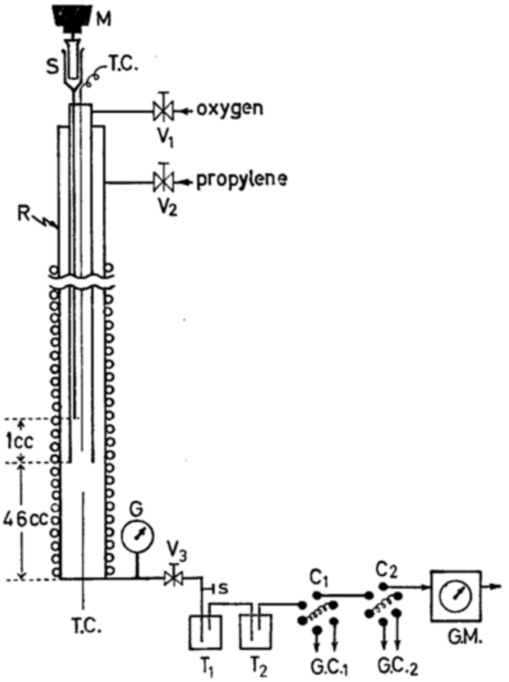

Fig. 2. Flow sheet of reaction apparatus for Exp. B.
C_1, C_2, sampling cock; G, press. guage (Bourdon type); G. $C._1$, G. $C._2$, gas chromatograph; G. M., wet gas meter; M, slow geared motor; R, reactor; S, syringe; s, sampling point; T. C., thermocouple; T_1, T_2, cold trap; V_1, V_2, V_3, needle valve

Procedures. *Exp. A* was carried out under 3.5 atm, using a reactant gas consisting of 80 vol% of propylene gas and 20 vol% oxygen. The linear velocity of the reactant gas was kept constant at 2.5 cm/sec on the empty-tube basis under the reaction conditions. The additives were fed into the mixer (kept about 80°C) by means of a glass syringe whose plunger was pushed at a constant speed using a slow-geared motor; the

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*[3] JIS SUS-27, AISI 304, Austenite.

additives were then mixed with the reactant gas. The concentrations of the additives varied a little as the reaction temperature changed; they were 0.61—0.83 vol% for acetaldehyde, 0.14—0.20 vol% for *t*-butyl hydroperoxide, and 0.55—0.65 vol% for propionaldehyde.

Exp. B was carried out under 3.0 atm. Propylene gas was passed through the outer tube. Allyl bromide (in Exp. B_1) or acetaldehyde (in Exp. B_2), which had been fed through the syringe needle was reacted with oxygen in the space (1.0 cc) of the inner tube. The reaction products from this space immediately reacted with propylene in the space (46 cc) of the outer tube. The flow rates of the reactants (at a normal temperature and pressure in the vapor phase) were as follows; allyl bromide, 1.14 *l*/hr, oxygen, 1.05 *l*/hr, and propylene gas, 4.26 *l*/hr, for the experiments (Exp. B_1) at 340 and 280°C, acetaldehyde, 1.17 *l*/hr, oxygen, 0.9 *l*/hr and propylene gas, 5.6 *l*/hr, for the experiment (Exp. B_2) at 280°C, and acetaldehyde, 1.17 *l*/hr, oxygen, 1.1 *l*/hr, and propylene gas, 5.8 *l*/hr, for the experiment (Exp. B_2) at 255°C.

Analysis. The reaction gas was analyzed gas chromatographically. An activated charcoal column of one meter long was used for oxygen, carbon monoxide, and methane at 50°C. A two-meter column containing activated alumina with 2 wt% of squalane was used for ethane and ethylene at 70°C (Exp. A) or 50°C (Exp. B). An eight meter column containing 30 wt% of acetonylacetone S on Celite 545 was used for oxygen + carbon monoxide + methane, ethane + ethylene, carbon dioxide, propane, and propylene at about 10°C. A three-meter column containing 30 wt% of Reoplex 400 on Celite 545 was used for acetaldehyde, propylene oxide, propionaldehyde, and acrolein at 70°C for Exp. A. A six-meter column containing 10 wt% of Reoplex 400 on Diasolid M was used at 50°C for Exp. B. All the packing materials except the Diasolid M were obtained from the Nishio Kogyo Co., Ltd. (Tokyo). The Diasolid M was obtained from the Nippon Chromato Kogyo Co., Ltd. (Tokyo).

The analytical procedures were the same as have been described before,[1] except that two sampling cocks were used for the analysis of the non-condensed gas sample in Exp. B.

Results and Discussion

The reactions studied are tabulated in Table 1.

Experiment A (Effect of a small amount of additives). In the case of Exp. A_0 (the oxidation experiment without additives), the oxidation reaction took place above 360°C.

Addition of t-Butyl Hydroperoxide. As Fig. 3 shows, the oxidation reaction took place above 300°C. Methane is much increased by the addition of *t*-butyl hydroperoxide, while there is only a small increase in ethane, as shown in Fig. 3. The increased methane formation shows the increased formation of the methyl radical. However, these methyl radicals probably contribute only a little to the formation of ethane by the recombination reaction. These observations show that the recombination of the radicals can be neglected in this reaction system because of the inhibiting effect of excess propylene, as the discussion of Mullen and Skirrow[6] has established.

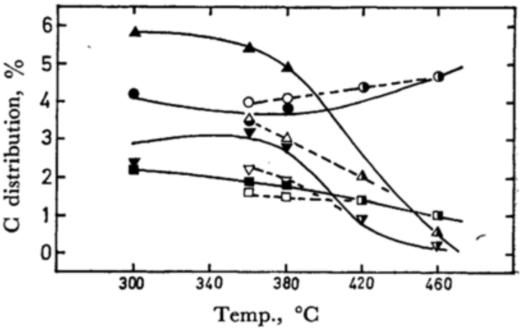

Fig. 3. Carbon distribution - temp. curves with the addition of *t*-butyl hydroperoxide; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_1).
-●- C_3H_8; --○-- C_3H_8 in Exp. A_0;
-■- C_2H_6; --□-- C_2H_6 in Exp. A_0;
-▲- C_2H_4; --△-- C_2H_4 in Exp. A_0;
-▼- CH_4; --▽-- CH_4 in Exp. A_0

TABLE 1. REACTIONS STUDIED IN THIS PAPER

Symbol	Additive	Reactor	Temp., °C	Amount of additive
Exp. A_0*	no additive	Fig. 1	360—460	
Exp. A_1	t-C_4H_9OOH	Fig. 1	300—460	0.14—0.20 vol%
Exp. A_2	CH_3CHO	Fig. 1	300—460	0.61—0.83 vol%
Exp. A_3	C_2H_5CHO	Fig. 1	360—460	0.55—0.65 vol%
Exp. B_0	no additive	Fig. 2	255, 280	
Exp. B_1	oxidation products of C_3H_5Br to C_3H_6	Fig. 2	340, 280	C_3H_5Br 1.14 *l*/hr,** O_2 1.05 *l*/hr, C_3H_6, 4.26 *l*/hr
Exp. B_2	oxidation products of CH_3CHO to C_3H_6	Fig. 2	280	CH_3CHO 1.17 *l*/hr,** O_2 0.9 *l*/hr, C_3H_6 5.6 *l*/hr
			255	CH_3CHO 1.17 *l*/hr,** O_2 1.1 *l*/hr, C_3H_6 5.8 *l*/hr

* Without special remarks, blank exp. (without additive) for exp. A_2 and A_3.
** At normal temperature and pressure in vapor phase.

Addition of Acetaldehyde or Propionaldehyde. As Figs. 4 and 7, 5 and 8, and 6 and 9 show, the oxidation reaction took place above 300°C upon the addition of acetaldehyde (AA); a good agreement is observed between the results of Exp. A_0 and Exp. A_2 (AA-added experiments) above 360°C. The chain-initiating radicals are easily produced by the addition of AA; therefore, the oxidation reaction took place at 300°C in Exp. A_2, unlike Exp. A_0. On the other hand, the amount of AA added is so small that the concentrations of the radicals in this reaction are not changed from those of Exp. A_0; therefore, the reaction courses and the results vary little upon the addition of AA above 360°C. Thus, AA may be concluded to be the branching agent in the case of excess propylene under pressure, as in the case of reduced-pressure experiments with a relatively low partial pressure of propylene.[3b,4-6] The apparent reaction times were kept constant in the Exp. A series; the results

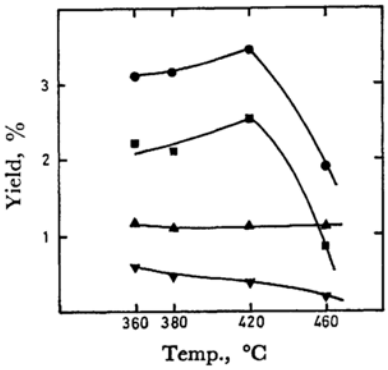

Fig. 4. Yield-temp. curves; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_0).
● AA ■ PO ▲ Acr ▼ PA

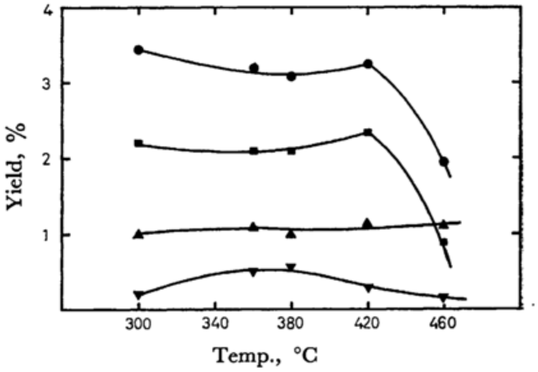

Fig. 7. Yield-temp. curves with the addition of AA; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_2).
● AA ■ PO ▲ Acr ▼ PA

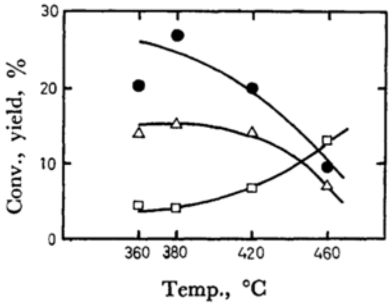

Fig. 5. Conv.- and yield-temp. curves; under 3.5 atm with mol fraction of O_2, 0.2 (exp A_0).
● conv. of C_3H_6 △ yield of CO
☐ yield of CO_2

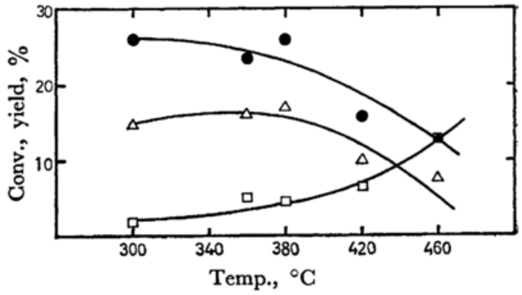

Fig. 8. Conv.- and yield-temp. curves with the addition of AA; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_2).
● conv. of C_3H_6 △ yield of CO
☐ yield of CO_2

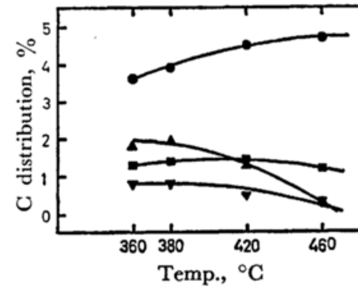

Fig. 6. Carbon distribution-temp. curves; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_0).
● C_3H_8 ■ C_2H_6 ▲ C_2H_4 ▼ CH_4

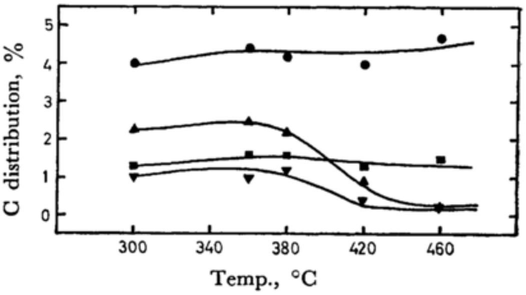

Fig. 9. Carbon distribution - temp. curves with the addition of AA; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_2).
● C_3H_8 ■ C_2H_6 ▲ C_2H_4 ▼ CH_4

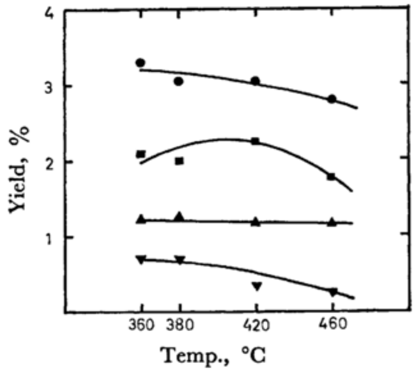

Fig. 10. Yield-temp. curves with the addition of PA; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_3).
▲ AA ■ PO ▲ Acr ▼ PA

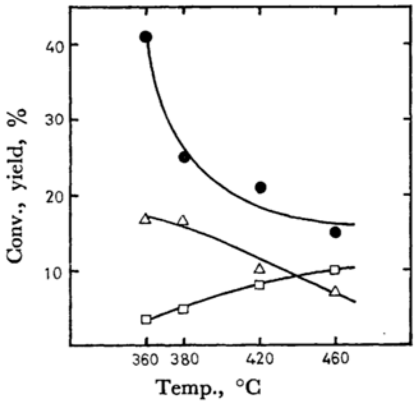

Fig. 11. Conv.- and yield-temp. curves with the addition of PA; under 3.5 atm with mol fraction of O_2, 0.2 (exp A_3).
● Conv. of C_3H_6 △ yield of CO
☐ yield of CO_2

TABLE 2. THE RESULTS OF Exp. B

	Temp. of outer tube °C	React. time sec		Conv. of O_2 %	Conc. (vol %) in products flow								
		inner tube	outer tube		AA	PO	PA	Acr	CO	CO_2	CH_4	C_2H_6	C_2H_4
Exp. B_1	340*	2.5	36	—	0.52	0.12	0.07	0.06	—	—	—	—	—
	280	2.7	40	20	0.52	0.06	0.06	0.04	2.6	2.0	0.51	0.13	0.20
Exp. B_2	280	2.8	34	52	—**	0.30	0.07	0.06	1.7	4.0	0.44	0.12	0.27
	255	2.8	34	51	—**	0.25	0.07	0.04	3.1	2.1	0.91	0.26	0.14

* The analysis of the gaseous products were failed.
** The analysis of AA was failed owing to the scale out of its peak.

of Exp. A_2 indicate that the induction period of this oxidation reaction was shortened by the addition of a small amount of AA between 300—360°C as has already been found in static experiments.[5,6]

Imamura *et al.* studied the addition of a large amount of AA in nearly the same reaction system as in Exp. A_2 at normal pressure.[12] They showed that the selectivity of acetic acid was four times that of PO (propylene oxide),[12] and also that acetic acid decreased and PO increased with a decrease in the amount of added AA.[12] In our work, the amount of added AA is very small, as shown in Table 1, and the rates of the oxidation reaction are found to be increased only a little, as has already been found in static experiments.[5,6] The addition of AA probably enhances the rates of all the reaction paths. The branching reaction is as follows.[17a]

$$CH_3CHO + O_2 \rightarrow CH_3\dot{C}O + \dot{O}OH$$

Figures 4 and 10, 5 and 11, and 6 and 12 show that upon the addition of propionaldehyde (PA) the oxidation reaction still takes place at 360°C (Exp. A_3) as in Exp. A_0, and also that the results of the two experiments Exp. A_0 and Exp. A_3 disagree with each other not only in the trend of the curves

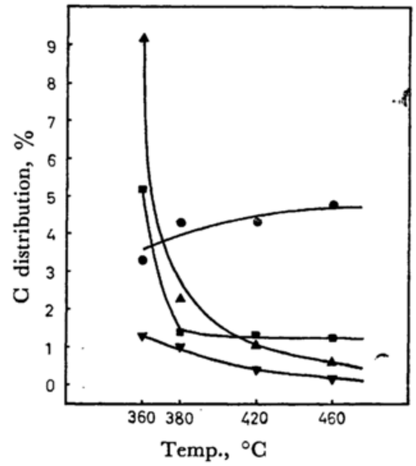

Fig. 12. Carbon distribution - temp. curves; with the addition of PA; under 3.5 atm with mol fraction of O_2, 0.2 (exp. A_3).
● C_3H_6 ■ C_2H_6 ▲ C_2H_4 ▼ CH_4

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12) J. Imamura, N. Nagato, S. Sato and N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1863 (1966).

but also in the numerical values. Thus, PA is not the branching agent in this reaction.

Experiment B. Table 2 contains the results of Exp. B. Exp. B_0 did not take place at 255, 280, and 340°C. Therefore, the products shown in Table 2 must be formed by the reactions of the species produced in the inner tube.

Experiment B_1 $(C_3H_5Br+O_2)+C_3H_6$. At 280°C, the amount of AA formed is about ten times those of PO, PA, and acrolein (Acr) as Tables 2 and 3 show.

TABLE 3. COMPARISION OF RELATIVE YIELD OF AA, PO, PA AND Acr IN Exp. B WITH THOSE IN Exp. A_0 (The values of Acr in each experiment is taken as unity.)*

	Temp., °C	AA	PO	PA	Acr
Exp. A_0 (Fig. 4)	380	2.9	1.9	0.44	1
Exp. B_1**	340	8.7	2.0	1.2	1
Exp. B_1**	280	13	1.5	1.5	1
Exp. B_2**	280	—	5.0	1.2	1
Exp. B_2**	255	—	6.3	1.2	1

* Acr is observed to be relatively insensitive oxygenated product to the variations of experimental conditions in comparision with AA and PO as shown in the previous paper[1] and Figs. 4, 7 and 10 in this paper.

** Calculated from the data presented in Table 2.

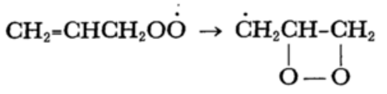
In this case, allyl bromide is decomposed into the allyl radical and the bromine atom.[13] The allyl radical produced most likely reacts with oxygen to form the allyl peroxy radical in the inner tube of the reactor. The allyl peroxy radical has been considered to be the main active species in the homogeneous-gas-phase oxidation of propylene.[3b,6,8] The bromine atom which is converted into bromine or hydrogen bromide most likely affects the course of the reaction. Bromine is an especially active catalyst for the decomposition of AA, according to Fromherz.[14] Hurst, Skirrow and Tipper[15] discussed the result of the oxidation of butene containing hydrogen bromide, citing some Russian workers results reporting the decomposing action of hydrogen bromide on hydroperoxide. Thus, the decomposition of AA, allyl hydroperoxide, and perhaps the allyl peroxy radical should all be considered here. The products described in Table 2 are, then, formed by the succeeding reactions of the allyl peroxy radical and the allyloxy radical. The alkoxy radical produced from the decomposition of peroxide is considered to decompose according to the following reactions:[16]

$$CH_2{=}CHCH_2\dot{O} \rightarrow CH_2{=}\dot{C}H + CH_2O$$
$$\searrow CH_2{=}CHCHO + \dot{H}$$

The same kinds of products are obtained in Exp. B_1 and Exp. A_0, while the oxidation reaction did not take place in Exp. B_0. Therefore, the reaction paths in the oxidation of propylene are not extinguished in Exp. B_1 by the presence of bromine or hydrogen bromide; furthermore, these paths start from the same active species, which are present in Exp. B_1 and Exp. A_0. The active species must be the allyl peroxy radical, because this is produced almost only in the inner tube of the reactor (as Exp. B_0 shows, the oxidation reaction without an additive did not take place), and also because the presence of the allyl peroxy radical as an active species in the oxidation of propylene is generally accepted.[3b] The secondary reactions induced by the radicals from the inner tube can be neglected at 280°C, because only a low conversion of oxygen is observed, as shown in Table 2.

The yield of AA relative to PO, PA, and Acr in Exp. B_1 at 280°C is higher than that of Exp. A_0, as Table 3 shows.

The above discussion leads to the conclusion that only the allyl peroxy radical contributes to the formation of AA. Shtern and Polyak[3b] and Neiman *et al.*[3b] proposed, and demonstrated kinetically, the following scheme for the formation of AA:

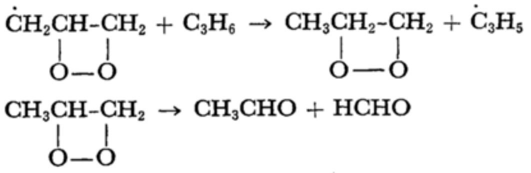


$$CH_2{=}CHCH_2O\dot{O} \rightarrow \dot{C}H_2\underset{\underset{O}{|}}{C}H\text{-}\underset{\underset{O}{|}}{C}H_2 \quad (O{-}O)$$

$$\rightarrow \dot{C}H_2CHO + HCHO$$

$$\dot{C}H_2CHO + C_3H_6 \rightarrow CH_3CHO + \dot{C}_3H_5$$

This scheme does not contradict the results of Exp. B_1 at 280°C. Thus, it is reasonable to conclude that AA is formed by the isomerization of the allyl peroxy radical, as in Shtern and Polyak's scheme. The following modification may be suggested for this scheme, considering the propylene excess atmosphere:



$$\dot{C}H_2\underset{\underset{O}{|}}{C}H\text{-}\underset{\underset{O}{|}}{C}H_2 + C_3H_6 \rightarrow CH_3\underset{\underset{O}{|}}{C}H_2\text{-}\underset{\underset{O}{|}}{C}H_2 + \dot{C}_3H_5$$

$$CH_3\underset{\underset{O}{|}}{C}H\text{-}\underset{\underset{O}{|}}{C}H_2 \rightarrow CH_3CHO + HCHO$$

The allyl peroxy radical is most likely to be formed

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[13] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Vol. 1. Reinhold Pub. Corp., New York (1954), p. 260.

[14] H. Fromherz, *Z. physik. Chem.*, **B25**, 301 (1934).

[15] P. Hurst, G. Skirrow and C. F. H. Tipper, *Proc. Roy. Soc.*, **A268**, 405 (1962).

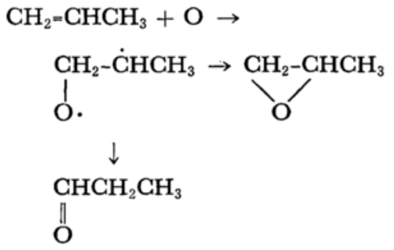
[16] K. Maruyama, *Kagaku (Chemistry)*, **21**, (No. 11) 54 (1966).

according to the following scheme, as proposed by Shtern and Polyak[3b] for the oxidation of propylene;

$$\mathrm{CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CH\dot{C}H_2 + \dot{O}OH}$$

$$\mathrm{CH_2{=}CH\dot{C}H_2 + O_2 \rightarrow CH_2{=}CHCH_2O\dot{O}}$$

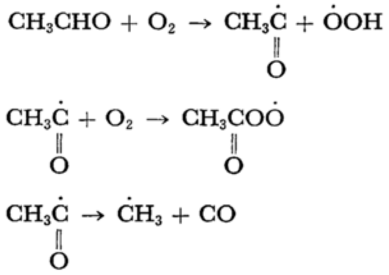
Contrary to the results of Exp. A_0, PO is formed in an amount comparable to PA and Acr at 280°C, as shown in Tables 2 and 3.*4 According to the above discussion concerning the formation of AA, allyl peroxy radical is the sole active oxygenated species formed in the inner tube, from which the oxygenated products are derived. The increased relative yield of PA in Exp. B_1 at 280°C may be compared with the small relative yield of PA in Exp. A_0 (Table 3). This fact strongly suggests that the reaction path to PA is emphasized by the presence of the allyl peroxy radical. The yield of PO is comparable to the yield of PA, as shown in Table 3. Cvetanović proposed the rearrangement of the oxygeneated biradical to PO and PA in the reaction of propylene and an oxgen atom as follows,[10] (he obtained almost equal amounts of PO and PA):



Our results can also be explained well on the basis of Cvetanović's mechanism; *i. e.*, the allyl peroxy radical contributes to the formations of PO and PA to an equal extent. Since the allyl peroxy radical is the sole active species, as has been established above, the contribution of the allyl peroxy radical to the formation of Acr is considered to be feasible according to the discussion of Mullen and Skirrow.[6] The yield of Acr comparable to those of PO and PA (Table 3) suggests the same degree of contribution of the allyl peroxy radical to the reaction paths which produce the said three products. To summarize the above discussions, the allyl peroxy radical is the sole precursor of AA, and it also contributes to the formation of PO, PA, and probably Acr to almost equal extents. At a higher temperature (340°C), the amount of PO becomes greater than those of PA and Acr in Exp. B_1, as shown in Table 2. This result may be ascribed to the further reaction of AA, as will be discussed below.

Experiment B_2 $(CH_3CHO+O_2)+C_3H_6$. In the case of Exp. B_2, the amounts of PO produced are greater than those of PA and Acr at 225 and 280°C, as shown in Tables 2 and 3. As has already been described, at the same temperature of 280°C, the amount of PO produced is comparable to those of PA and Acr (Table 2) in Exp. B_1. In Exp. B_2, the relative amount of PO is greater than that in Exp. A_0 (Table 3). The concentration of AA in the inner tube in Exp. B_1 at 280°C should be much less than that of Exp. B_2. These facts show that the contribution of the oxidation product of AA to the formation of PO is superior to that of the allyl peroxy radical.

Here, AA is easily oxidized to the acetyl peroxy radical,[17a18] its oxidation scheme is as follows;[17a,18].

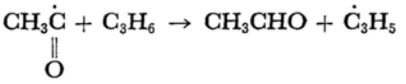


$$\mathrm{CH_3CHO + O_2 \rightarrow CH_3\underset{\underset{\displaystyle O}{\|}}{\dot{C}} + \dot{O}OH}$$

$$\mathrm{CH_3\underset{\underset{\displaystyle O}{\|}}{\dot{C}} + O_2 \rightarrow CH_3\underset{\underset{\displaystyle O}{\|}}{C}O\dot{O}}$$

$$\mathrm{CH_3\underset{\underset{\displaystyle O}{\|}}{\dot{C}} \rightarrow \dot{C}H_3 + CO}$$

In the propylene-excess atmosphere, the acetyl radical formed will react with propylene;



$$\mathrm{CH_3\underset{\underset{\displaystyle O}{\|}}{\dot{C}} + C_3H_6 \rightarrow CH_3CHO + \dot{C}_3H_5}$$

Thus, it is reasonable to suggest that the most reactive radical in the above scheme—the acetyl peroxy radical—plays an important role in the main reactions in Exp. B_2.

Imamura *et al.* studied the same reaction system as in Exp. B_2 with lower oxygen under normal pressure at 180 and at 270°C.[12] Their reaction gas consisted of about 0.4 AA and about 0.2 air in the inner reactor and of about 0.4 propylene in the outer reactor.[12] They used a reactor, the reaction spaces of which were 135 m*l* for the inner reactor

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*4 The data presented in Exp. B_1 of Table 2 show an increase in PO, PA and Acr with an increase in the temperature; this indicates a negligible interaction between these products and the allyl bromide or species derived from them. The known reactions of PO with allyl bromide, bromine and hydrogen bromide can be neglected under the conditions of Exp. B_1, such as the reaction time of 36—40 sec and the reaction tmeperature of 280—340°C [P. Bedos, *Compt. rend.*, **183**, 562 (1926); A. Rosowsky, "Heterocyclic Compounds with Three- or Four-membered Rings" (A. Weissberger, ed.), Part 1, Interscience Pub. New York (1964), pp. 436—455].

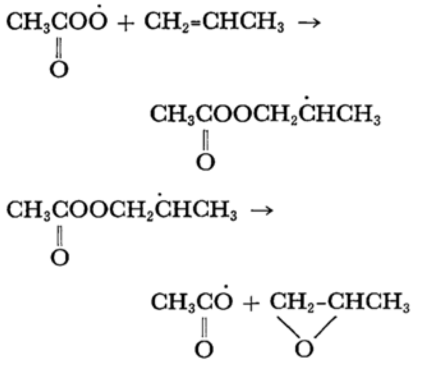
17) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Japanese translation by T. Kwan and A. Matsuda, Vol. 1, 17a) p. 81, 17b) Chap. 7 § 2, 17c) Chap. 1 § 7, Iwanami Shoten, Tokyo (1963).

18) G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Chap. 5, Butterworths Co., London (1962).

and 265 m*l* for the outer reactor; the outlet of the inner reactor had a narrow neck. They obtained considerable amounts of acetic acid, and peracetic acid and a small amount of PO. This supports the formation of the acetyl peroxy radical in Exp. B_2.

During the oxidation of propylene, PO retains the carbon skelton of propylene, according to the results of White, Davis and Hammack.⁹⁾ It has been proposed by Cvetanović¹⁰⁾ that PO is formed through the addition of an oxygen atom to the double bond of propylene. Oba and Sakai recently demonstrated that the methyl group of propylene is retained in PO in a homogeneous oxidation of propylene.¹¹⁾ These results indicate that PO is formed by the addition of active species to the double bond of propylene. Concerning the active species which may introduce the oxygen atom to the double bond of propylene, there have been no definite discussions which have experimental support about gas-phase homogeneous reactions. Only the acetyl peroxy radical and acetyl hydroperoxide have been proposed by Imamura *et al.* on the basis of their experiments,¹²⁾ and they evaluated these reaction paths low because of the low selectivity of the PO formation. It is reasonable to assume that the molecular reaction of acetyl hydroperoxide with propylene is very much slower than the addition of the acetyl peroxy radical to the double bond of propylene in the gas-phase reaction,¹⁷ᵇ⁾ because the addition of a radical to the double bond generally always proceeds with a low activation energy.¹⁷ᶜ⁾

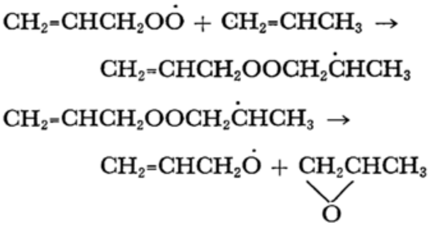
Therefore, the following scheme may be concluded to hold for the route to PO in Exp. B_2; it is deduced from the results of Exp. B_2 already described and also from the discussions presented above:



$$\underset{\substack{\|\\ O}}{CH_3CO}\dot{O} + CH_2{=}CHCH_3 \rightarrow \underset{\substack{\|\\ O}}{CH_3CO}OCH_2\dot{C}HCH_3$$

$$\underset{\substack{\|\\ O}}{CH_3CO}OCH_2\dot{C}HCH_3 \rightarrow \underset{\substack{\|\\ O}}{CH_3\dot{C}O} + \underset{\diagdown O \diagup}{CH_2\text{-}CHCH_3}$$

PO is formed in Exp. B_1 in an amount comparable with those of PA and Acr, which are minor products in Exp. A_0 (Table 2, Fig. 4). Furthermore, the amount of PO formed in Exp. B_1 is distinctly small in comparision with that formed in Exp. B_2 (Table 2). These observations strongly indicate that the contribution of the allyl peroxy radical to the formation of PO is less than that of the acetyl peroxy radical. The route *via* the addition of the allyl peroxy radical is as follows:

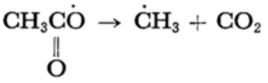


$$CH_2{=}CHCH_2O\dot{O} + CH_2{=}CHCH_3 \rightarrow CH_2{=}CHCH_2OOCH_2\dot{C}HCH_3$$

$$CH_2{=}CHCH_2OOCH_2\dot{C}HCH_3 \rightarrow CH_2{=}CHCH_2\dot{O} + \underset{\diagdown O \diagup}{CH_2CHCH_3}$$

Thus, the route *via* the addition of the acetyl peroxy radical may be concluded to be the main route for the formation of PO in the gas-phase homogenous oxidation of propylene.*5 This conclusion accords with the discussion presented in the previous paper,¹⁾ where the decomposition of the species containing an acetyl group was found to be retarded to some extent in an oxidation atmosphere with an excess of propylene.

The amount of PO increased at 340°C in comparison with the amount at 280°C in Exp. B_1 (Table 2); this fact indicates that the route *via* the acetyl peroxy radical becomes predominant as the amount of AA increases with a rise in the temperature. PO is regarded as a stable species under normal reaction conditions, according to the results of Kamiya.¹⁹⁾ The acetoxy radical produced will decompose as follows.¹⁸⁾ Here, Kamiya's results indicate the low formation of acetic acid in the same reaction system.²⁰⁾



$$\underset{\substack{\|\\ O}}{CH_3C}\dot{O} \rightarrow \dot{C}H_3 + CO_2$$

Two paths have been discussed for the formation of the methyl radical, *i. e.*, the decomposition of the acetyl radical and the decomposition of the acetyl oxy radical. On the basis of the low yield of methane, the methyl radical probably partly reacts with propylene to form methane and is partly burned to carbon dioxide. Therefore, it can not

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*5 The activation energy of the $CH_3CHO+O_2 \rightarrow CH_3\dot{C}O+\dot{O}OH$ reaction is 30 kcal/mol, and that of the $C_3H_6+O_2 \rightarrow C_3H_5+\dot{O}OH$ reaction is also about 30 kcal/mol or somewhat higher, according to the data tabulated in Semenov's book (N. N. Semenov, *loc. cit*, p. 268 and other parts). The reaction temperature is 360—460°C in Exp. A_0 and 255 or 280°C in Exp. B_2. These suggest that the concentration of the hydroperoxy radical in Exp. A_0 is not lower than that in Exp. B_2. A comparison of the yield of PO relative to those of PA and Acr in Exp. A_0 with that in Exp. B_2 reasonably suggest that the contribution of the hydroperoxy radical to the formation of PO is very small. On this point, Imamura *et al.* neglected the contribution of the hydroperoxy radical to the formation of PO, though they considered the formation of the hydroperoxy radical in their work.¹²⁾

19) Y. Kamiya, *Sekiyu Gakkai Shi (J. Japan Petrol. Inst.)*, **5**, 573 (1962).

20) Y. Kamiya, *ibid.*, **5**, 398 (1962).

be decided which path is major. The allyloxy radical produced is considered to be energy-rich and to decompose as follows:[16)]

$$CH_2{=}CHCH_2\dot{O} \rightarrow CH_2{=}\dot{C}H + HCHO$$

The formation of allyl alcohol is neglected, because it could not be detected in Exp. A_0.

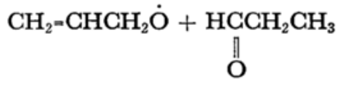
Formation Reactions of PA and Acr. Comparable amounts of PO, PA and Acr were formed in Exp. B_1 at 280°C.

PA and Acr are also formed in Exp. B_2; this fact may be attributed to the secondary reaction by the allyl peroxy radical formed from radicals induced by the oxidation or decomposition of AA. This idea is supported by the higher conversion of oxygen (50%) in Exp. B_2 than that in Exp. B_1 (20%). According to the discussions presented in the preceding section (in Exp. B_1), the allyl peroxy radical is responsible for the formation of PA and probably of Acr also.

PA retains the carbon skelton of propylene during the reaction, according to the results of White, Davis and Hammack.[9)] Cvetanović[10)] has proposed that PA is formed through the isomerization of the oxygenated biradical which is formed by the addition of an oxygen atom to the double bond of propylene. Here, the following similar isomerization of the oxygenated radical may be suggested for the formation of PA:

$$CH_2{=}CHCH_2OOCH_2\text{-}\dot{C}HCH_3 \rightarrow CH_2{=}CHCH_2OO\dot{C}H\text{-}CH_2CH_3$$

$$CH_2{=}CHCH_2OO\dot{C}H\text{-}CH_2CH_3 \rightarrow$$



$$CH_2{=}CHCH_2\dot{O} + \underset{\underset{O}{\|}}{HC}CH_2CH_3$$

It can be considered that an acetyl peroxy compound is more unstable than an alkyl peroxy compound. Therefore, this may be a reason for ruling out the route for the formation of PA[*6] *via* the addition of an acetyl peroxy radical.

Acr may be formed by the following decomposition of the allyloxy radical,[16)] as has been discussed above:

$$CH_2{=}CHCH_2\dot{O} \rightarrow CH_2{=}CHCHO + \dot{H}$$

The allyloxy radical is formed in line with the formation of part of PO (from allyl peroxy radical) and PA, as has been discussed above, so the yield of Acr should be less than twice the yield of PA. However, this is not satisfied in Exp. A_0 as shown in Fig. 4. This perhaps indicates that this reaction is minor. The yield of Acr in Exp. B_1 at 280°C is too low in view of the yields of PO and PA (Table 2). Therefore, this reaction is perhaps not feasible. The reaction *via* allyl hydroperoxide is considered to be feasible, however, the following reactions have been proposed by Mullen and Skirrow[6)] and also by Kamiya, Sekine and Yamakawa[8)] for the formation of Acr:

$$CH_2{=}CHCH_2O\dot{O} + C_3H_6 \rightarrow CH_2{=}CHCH_2OOH + \dot{C}_3H_5$$

$$CH_2{=}CHCH_2OOH \rightarrow CH_2{=}CHCHO + H_2O$$

The same scheme may be suggested for the formation of Acr.

Formation Reactions of Ethylene. White, Davis and Hammack[9)] have proposed that ethylene is formed *via* the allyl radical. Ethylene is considered to be formed according to the following reactions, which are the competing reaction in the formation of AA by Shtern and Polyak:[3b)]

$$CH_2{=}CHCH_2O\dot{O} \rightarrow CH_2{=}CH\dot{C}HOOH$$

$$CH_2{=}CH\dot{C}HOOH \rightarrow CH_2{=}\dot{C}H + CO + H_2O$$

The same scheme may be suggested for the formation of ethylene.

Though $CH_2{=}\dot{C}H$ is also formed from the decomposition of the allyloxy radical, as has been described above, the reaction path through the isomerization of the allyl peroxy radical is considered to be predominant on the basis of the low contribution of the allyl peroxy radical to the formation of PO, and also on the basis of the low yield of PA in Exp. A_0. $CH_2{=}\dot{C}H$ most likely reacts with propylene to form ethylene.

Two paths have been discussed for the formation of carbon monoxide, *i. e.*, the decomposition of the acetyl radical and the decomposition of $CH_2{=}CH\dot{C}HOOH$. There is no experimental evidence, however, upon the basis of which to decide which path is major.

Formation Reaction of Water. It has been postulated that the hydroperoxy radical are formed in the course of the initiation reaction. The following reactions most likely proceed in the formation of water:

$$HO\dot{O} + C_3H_6 \rightarrow HOOH + \dot{C}_3H_5$$

$$HOOH \rightarrow 2\dot{O}H$$

$$\dot{O}H + C_3H_6 \rightarrow H_2O + \dot{C}_3H_5$$

The Scheme of the Oxidation of Propylene in a Propylene-excess Atmosphere. To summarize the above discussions, a reaction scheme is

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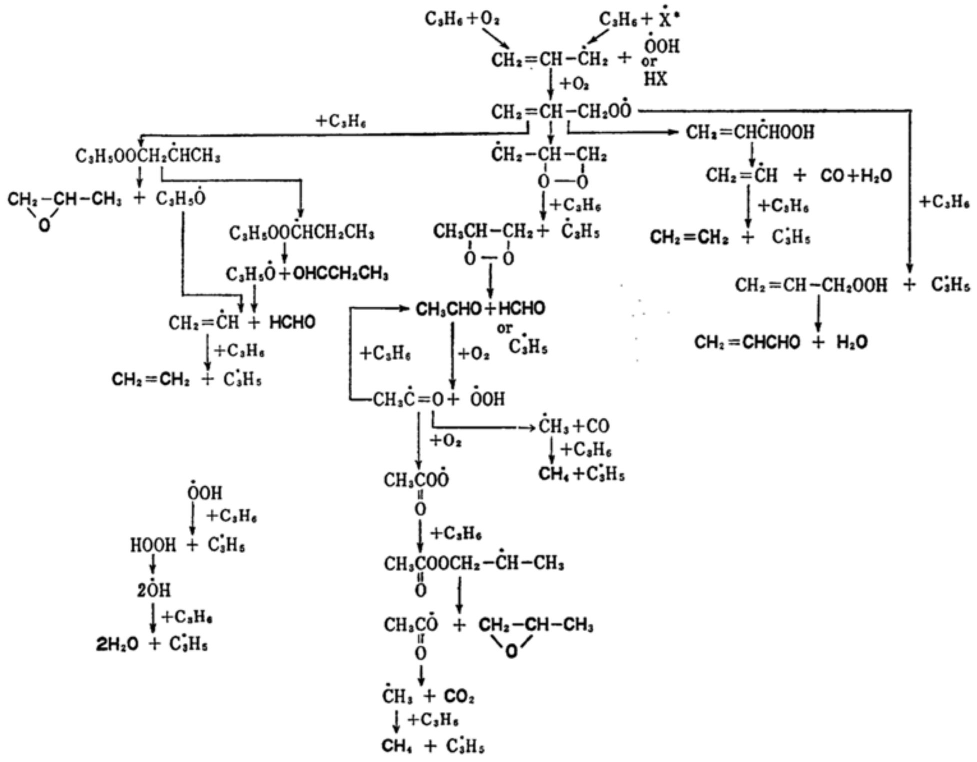
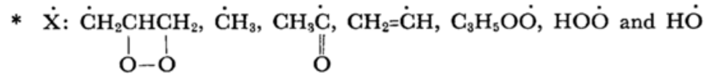
[*6] The yield of PA relative to Acr is lower in Exp. A_0 than that in Exp. B_1, where the concentration of the hydroperoxy radical is very small. Therefore, the contribution of the hydroperoxy radical to the formation of PA is neglected.

TABLE 4. THE PROPOSED REACTION SCHEME (main courses)





$* \ \dot{X}$: $\underset{|\quad\ |\ \ }{\underset{O-O}{\dot{C}H_2CHCH_2}}$, $\dot{C}H_3$, $CH_3\underset{\underset{O}{\|}}{\dot{C}}$, $CH_2{=}\dot{C}H$, $C_3H_5O\dot{O}$, $HO\dot{O}$ and $H\dot{O}$

presented in Table 4. Because of the propylene-excess atmosphere, propylene behaves as the hydrogen donor for the radicals, which are $\dot{C}H_3$ and $CH_2{=}\dot{C}H$.

The scheme presented in Table 4 is proposed for the main route of the oxidation of propylene. Though this scheme is supported by reasonable evidence in the main, other evidence will be necessary before this scheme can be regarded as a "theory" which can explain the phenomena accompanying the oxidation of propylene.

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